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USASRD L Technical Report 2196

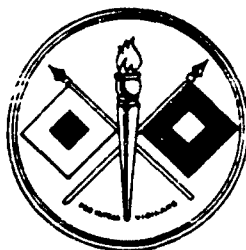
PROPERTIES OF HOT-PRESSED BARIUM TITANATE

by

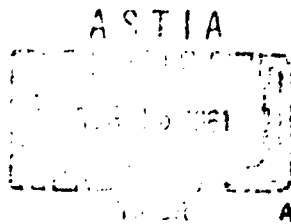
Arthur Brown

and

Robert Fischer



April 1961



U.S. ARMY SIGNAL RESEARCH AND DEVELOPMENT LABORATORY

FORT MONMOUTH, N. J.

April 1951

USASRDL Technical Report

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DA TASK NR. 3A99-15-001-01

U. S. ARMY SIGNAL RESEARCH AND DEVELOPMENT LABORATORY
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PROPERTIES OF HOT-PRESSED BARIUM TITANATE

INTRODUCTION

The objective of the program described was to develop a technique for producing a dense, hot-pressed barium titanate sample having an average grain size of less than one micron and to compare its electrical properties with those of conventionally-fired barium titanate.

Barium titanate had been hot-pressed by others using graphite dies. Hot-pressing it results in reduced barium titanate ceramic which, upon subsequent oxidation, was subject to grain growth. Hot-pressing of cadmium niobate in ceramic dies had previously been demonstrated at USASRD by DeBretteville, et al,¹ and barium titanate had been hot-pressed and some properties reported by Tennery.²

Further development of the hot-pressing technique has enabled the authors to produce nonreduced samples of extremely fine grain structure whose electrical properties are of interest.

METHOD

The hot-pressing apparatus consists of an induction furnace used in conjunction with a die assembly. An over-all view of the assembled apparatus is shown in Figure 1.

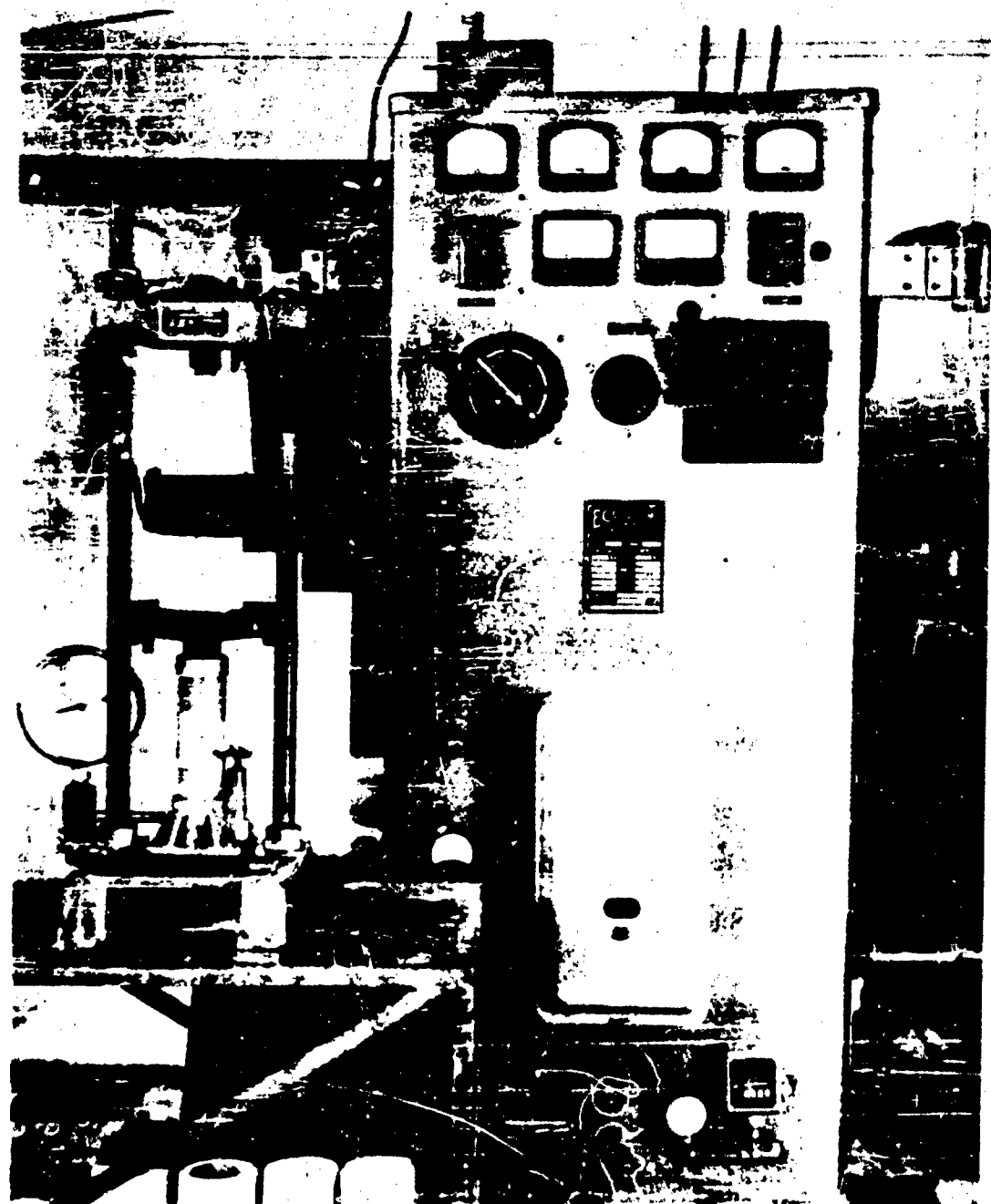
The induction power supply is a 20-kw, 10-kc motor generator, which allows rapid heating with good control. The furnace, which was assembled on the platen of the press, was a refractory fire brick cut to fit inside the induction coil and around the die assembly. A manual, manually-operated hydraulic laboratory press was used. The furnace and die assembly are shown in Figure 2.

The ceramic dies which have proven most effective for our work with barium titanate 100%, stabilized zirconia made slightly porous to improve thermal shock resistance. Other materials such as alumina and alumina porcelains can also be used with some degree of success. A stainless steel bushing was shrunk onto the ceramic sleeve to serve as the susceptor and mechanical support.

The method used to prevent adherence of the material being pressed to the ceramic die was to embed the sample in a relatively coarse zirconia powder (TAM No. 45006). This method prevented sticking to the die and allowed the sample to be ejected easily while hot. The amount of zirconia that diffused into the sample during firing has not been determined, but the layer of zirconia that adhered to the surface of the sample was easily removed by grinding.

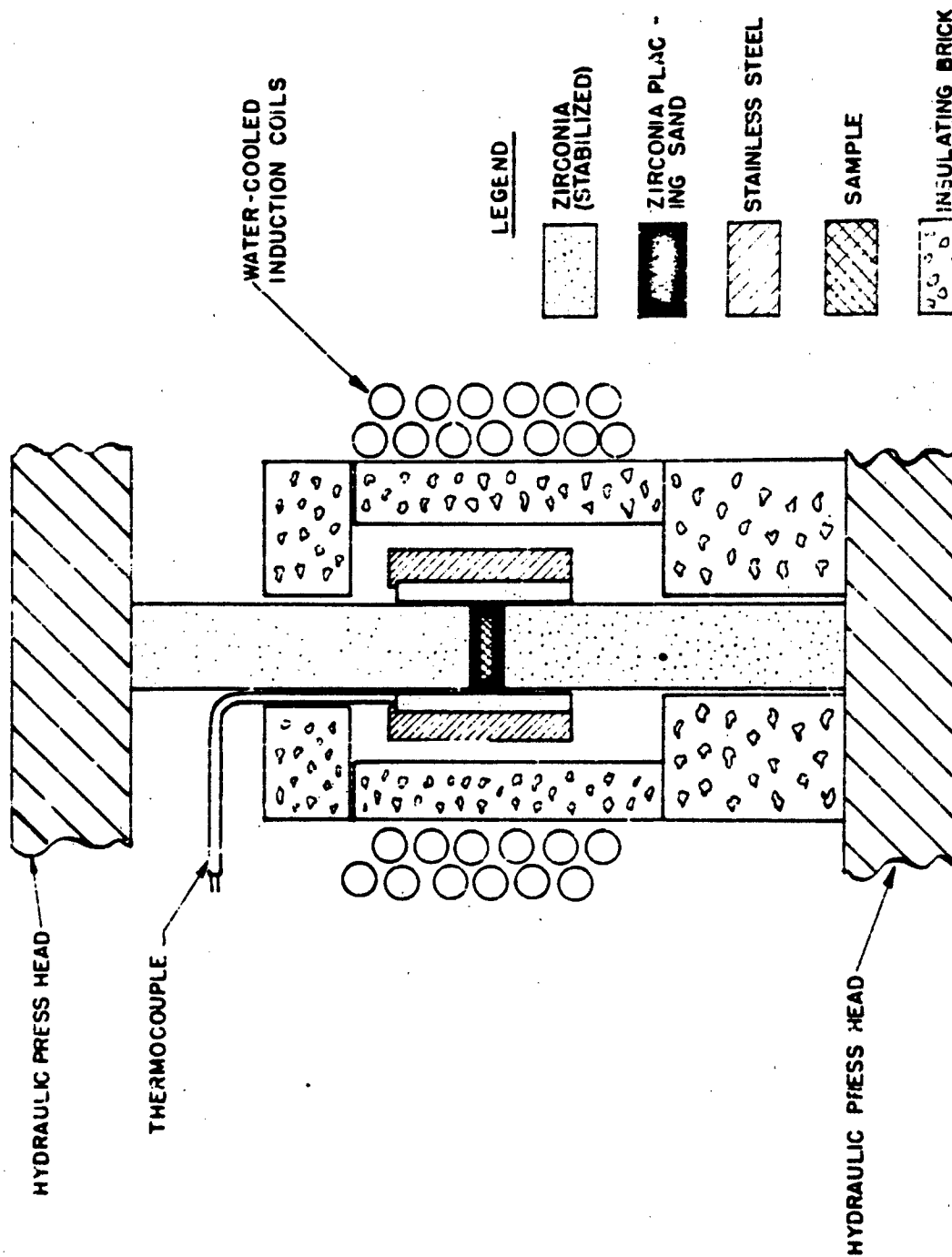
PROCEDURE

A sample disc of barium titanate 1/8 inch smaller in diameter than the zirconia die was preformed at 10,000 psi with no binder. This preformed disc was loaded into the hot-press in such a manner as to be completely encapsulated in zirconia placing sand. The loader was aligned in the induction coil, and a pressure of 5000 psi was applied and maintained out the heating cycle. The rate of heating was controlled in such a manner that a temperature of 2000° F was reached in ten minutes. The sample was held at this temperature and pressure twenty minutes and then quickly ejected from the die and buried in vermiculite to cool. After cooling, the sample was removed from its zirconia casing, ground to the desired shape, and polished.



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FIG 1 HOT-PRESSING APPARATUS



Other combinations of pressure, time, and temperature of firing were investigated; however, pressures above 5000 psi lead to rapid deterioration of the dies, and a significantly lower temperature or shorter time does not yield a fully vitrified body.

CHARACTERISTICS OF HOT-PRESSED BaTiO_3

Density and Microstructure

The polished samples had a yellowish color that is characteristic of nonreduced barium titanate. Fractured surfaces were glassy, an indication of the high density and fine grain size. Density measurements, made by displacement, averaged 5.9 gm/cc, some samples measuring as high as 6.0 gm/cc. When examined under 500 X magnification, polished samples exhibited no apparent grain structure before or after etching.

After careful polishing, samples were etched in a solution of 0.5% HF and 1.0% HNO_3 , and platinum shadowed carbon backed replicas were prepared and examined with the electron microscope at magnifications up to 20,000 X. It was found that due to the small grain size a satisfactory polishing and etching technique could not be developed.

Fractured surfaces were replicated and all electron micrographs are of unetched fractured surfaces. The grain size in the hot-pressed barium titanate was found to be less than 1 micron (Figure 2). Figure 4 illustrates the grain size observed in a fractogram of kiln-fired barium titanate.

The fine microstructure observed in the hot-pressed samples is attributed to the fine particle size of the starting material, and to the predominance of plastic flow as the mechanism of sintering under these conditions. The average particle size of the barium titanate used (TAM IT grade) was 0.5 micron. These particles were found to be agglomerated in such a manner that they indicated a particle size distribution of 1 to 5 microns by sedimentation methods. Electron micrographs showed the actual particles to be 1 micron and less (see Figure 5), essentially the same size as those appearing in the hot-pressed samples.⁸ This indicates that there was no significant grain growth during densification and that hot-pressing offers a method to be used to control grain size.

Electrical Characteristics

The electrical properties of hot-pressed barium titanate samples prepared as above were quite striking when compared to those of conventionally prepared samples. The dielectric strength has been found to be 500 volts per mil as compared with values of 100 to 200 volts per mil, usually observed in conventionally processed barium titanate samples 1/16 inch thick.

Figure 6 illustrates the differences observed in measurements of the dielectric constant and dissipation factor with temperature. The reduction in the peak of the dielectric constant in the vicinity of the Curie temperature is attributed to the fine grain size. At room temperature the dielectric constant is above 4000 and is independent of the orientation of the sample with respect to the direction of the former pressure. No dependence of K on frequency was found from 100 cps to 10 mc. Figure 7 depicts the variation of dielectric constant with time under static room temperature conditions for conventional and hot-pressed BaTiO_3 . The samples were deaged by heating to 200°C for 2 minutes; aging time was measured from the moment of removal from the oven. Since the aging of the dielectric constant has been reported to be due to a gradual reorientation of the ferroelectric domains, the results of this test are consistent with the fact that the domains in the hot-pressed material were relatively stable.^{9,10} The long-term stability has not been studied in conventional K₁ bodies.

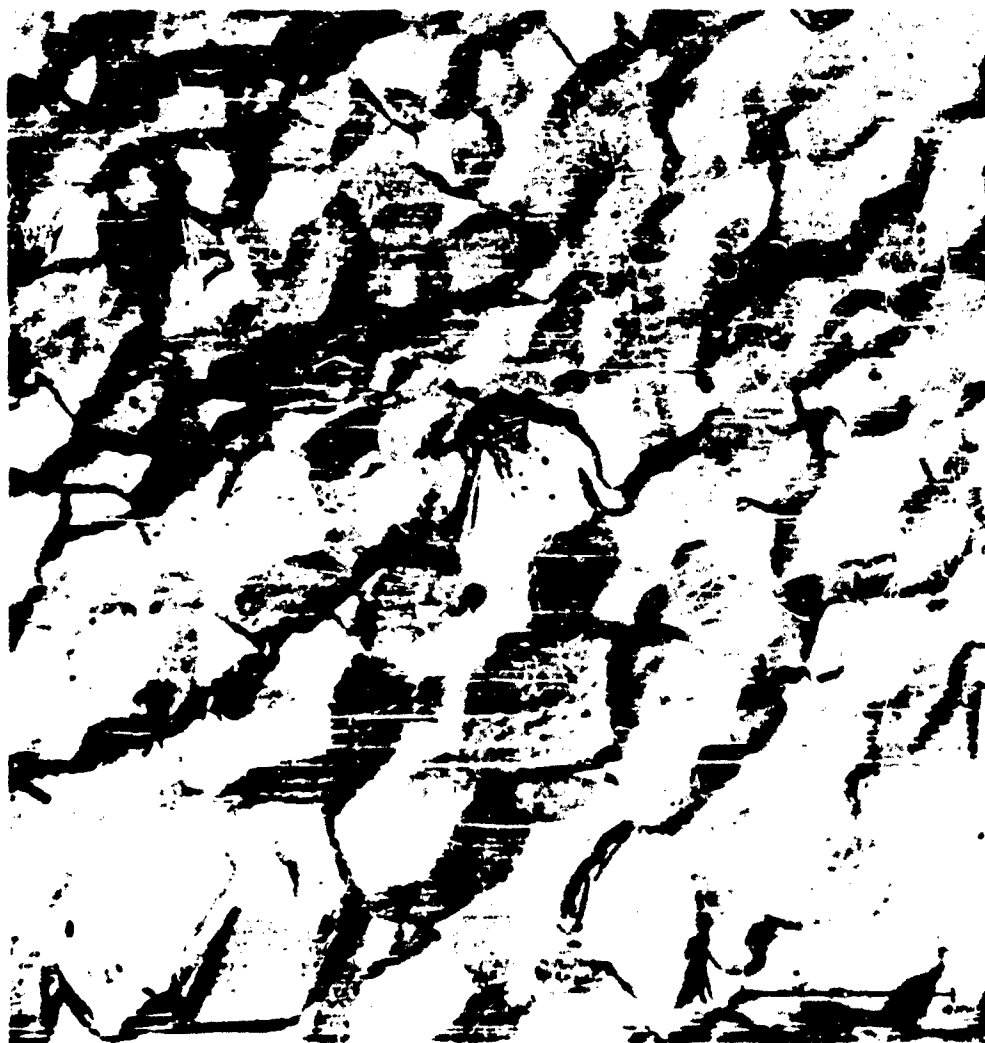


FIG 3 FRACTURED SURFACE OF HOT-
PRESSED BaTiO_3



FIG 4 FRACTURED SURFACE OF KILN-
FIRED BaTiO₃

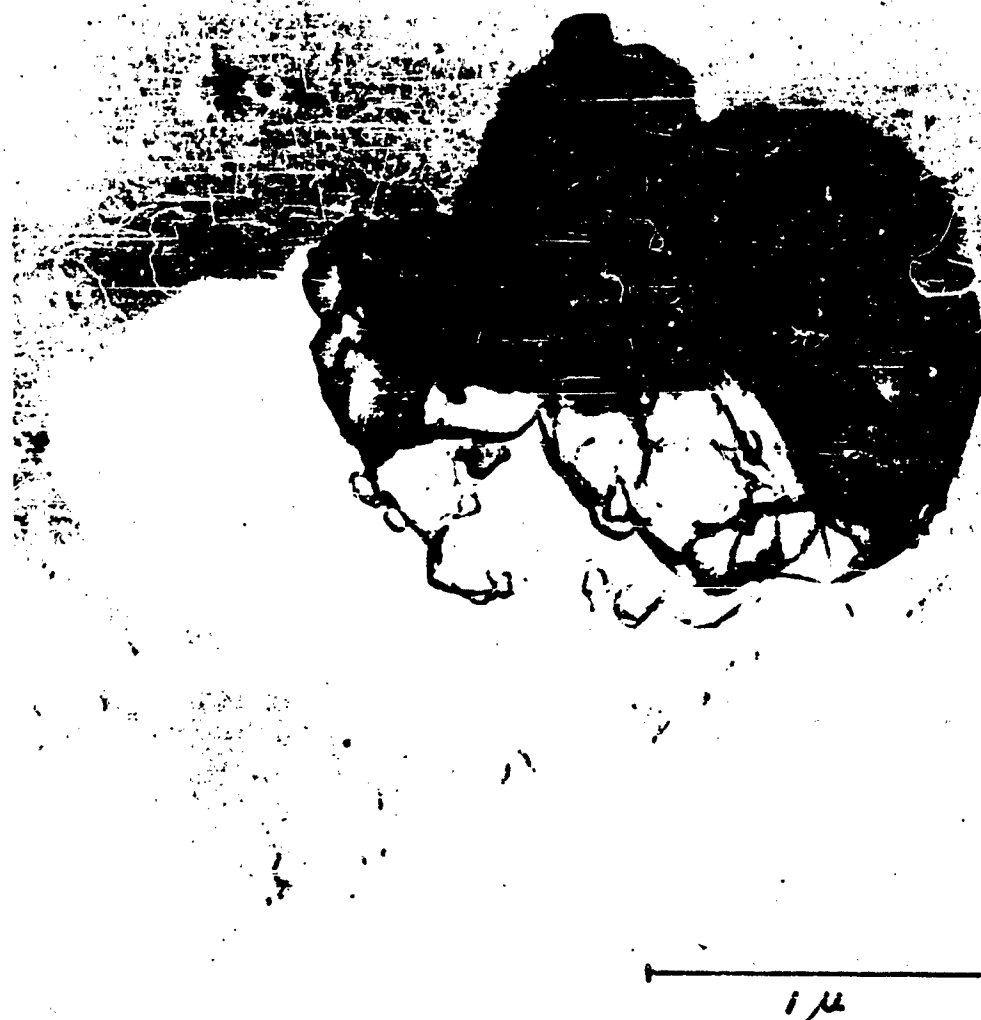


FIG 5 PARTICLE REPLICA OF BaTiO_3
POWDER

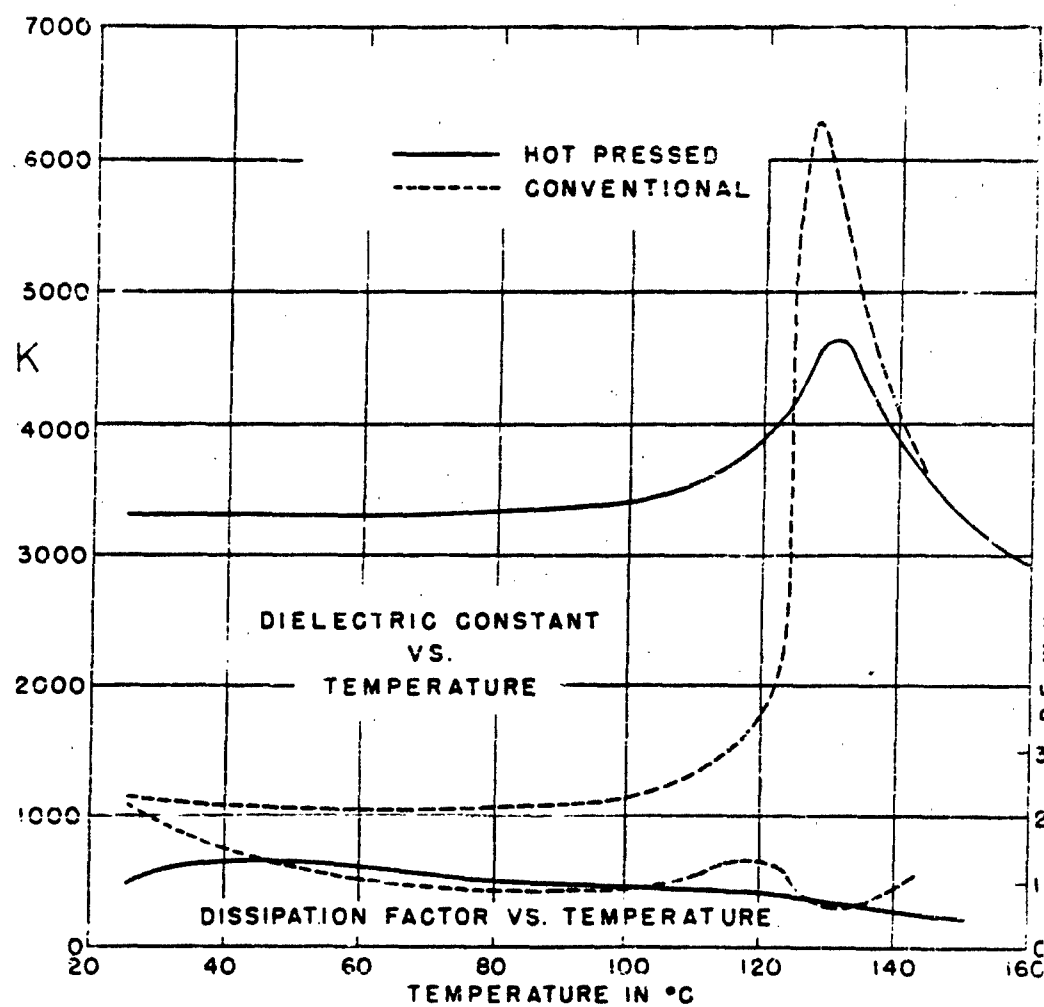
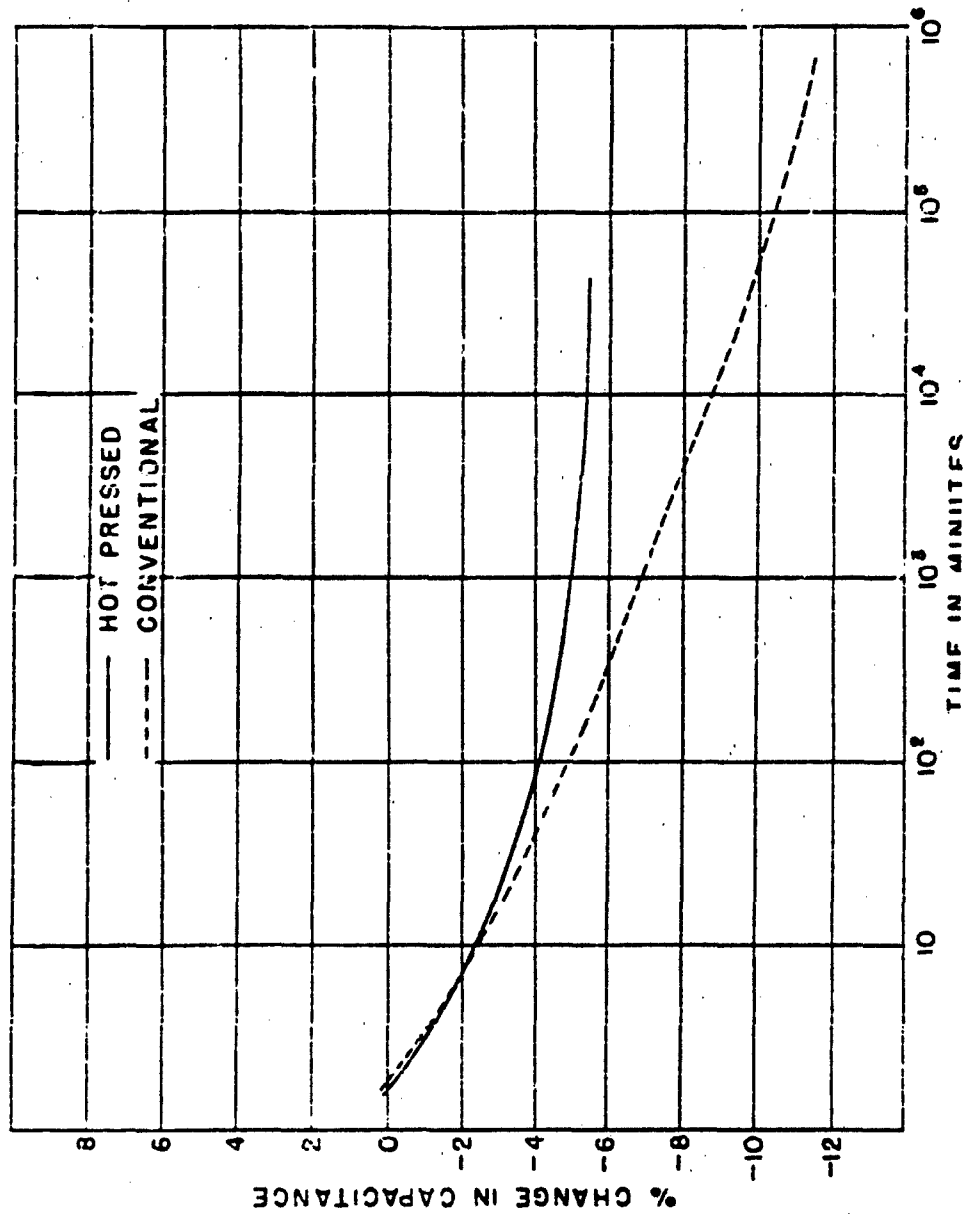


FIG 6

DIELECTRIC PROPERTIES OF TWO TYPES OF BARIUM TITANATE



An attempt was made to pole hot-pressed samples of BaTiO_3 by applying a high DC field at room temperature or while cooling from 120°C , but little or no piezoelectric response was observed.

CONCLUSIONS

The hot-pressing technique described in this report produced a dense, nonreduced barium titanate sample with no apparent grain growth. The limiting factor in producing a fine-grained BaTiO_3 body was in the particle size of the raw materials. A project has been initiated to produce a BaTiO_3 powder with an average particle size of less than 0.1 micron.

The dielectric properties of these materials were greatly enhanced by small crystallite size, but the piezoelectric response was almost completely eliminated. These results show the significance of the effect of density and grain size on the ferroelectric properties of barium titanate and indicate that an extension of this study over a wider range of particle sizes, particularly below 0.1 micron, might be expected to produce new or improved electrical properties in ferroelectric materials.

ACKNOWLEDGMENTS

The authors are grateful to John Charlton and Anne Dunlap of the Inorganic Dielectrics Team for compiling all the electrical measurements; to Sam DiVita and Ronald Brandmayr of the Inorganic Dielectrics Team and Nelson Terhune, former Chief of the Inorganic Dielectrics Team, for their guidance and assistance in preparing this report; and to Charles Cook, Jr., of the Exploratory Research Division "E" for the instructions in electron microscopy.

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